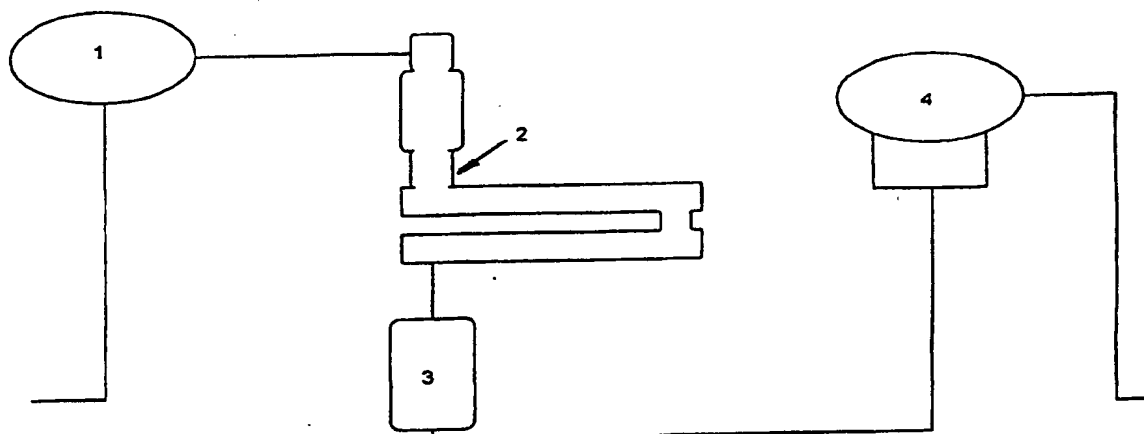




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21C 9/153, 9/16	A1	(11) International Publication Number: WO 97/01667 (43) International Publication Date: 16 January 1997 (16.01.97)
<p>(21) International Application Number: PCT/SE96/00882</p> <p>(22) International Filing Date: 1 July 1996 (01.07.96)</p> <p>(30) Priority Data: 9502365-1 29 June 1995 (29.06.95) SE</p> <p>(71) Applicants (for all designated States except US): SUNDS DEFIBRATOR INDUSTRIES AB [SE/SE]; S-851 94 Sundsvall (SE). SCA Graphic Research AB [SE/SE]; P.O. Box 3054, S-850 03 Sundsvall (SE).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): ANNERGREN, Göran [SE/SE]; Granbacken 14, S-856 34 Sundsvall (SE). BOMAN, Maria [SE/SE]; Hagavägen 22 A, S-856 41 Sundsvall (SE). BOMAN, Rolf [SE/SE]; Hagavägen 22 A, S-856 41 Sundsvall (SE). NORDEN, Solveig [SE/SE]; Odalvägen 14, S-862 41 Njurunda (SE).</p> <p>(74) Agents: IVERSEN HASSELROT, Eva et al.; L.A. Groth & Co. KB, P.O. Box 6107, S-102 32 Stockholm (SE).</p>	<p>(81) Designated States: AU, BR, CA, CN, JP, NO, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report. With amended claims.</p>	

(54) Title: BLEACHING OF LIGNOCELLULOSIC PULP WITH OZONE AND PERACID



(57) Abstract

The present invention relates to a method of bleaching lignocellulosic fiber material in a combination step with ozone and peracid, such as peracetic acid, $Z_{HCPa}MC$. The invention preferably relates to the bleaching of sulphate pulp. The pulp is ozone treated in a HC step in an ozone reactor, whereafter the pulp is diluted with water or white water, and peracid is added prior to an MC bleaching tower with subsequent washing.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Bleaching of lignocellulosic pulp with ozone
and peracid.

The present invention relates to a method of bleaching lignocellulosic fiber material in a combination step with ozone and peracid, such as peracetic acid, $Z_{HC}Paa_{MC}$. The invention preferably is directed to the bleaching of sulphate pulp. The pulp is treated with ozone in an HC step in an ozone reactor, where after the pulp is diluted with water or white water, and peracid is added prior to a MC bleaching tower, with subsequent washing.

At commercial operation, ozone has recently been introduced as a bleaching chemical at the bleaching of pulp, in order to minimize the use of bleaching chemicals, and, respectively, to increase the bleaching without using chlorine chemicals by using a strong delignification chemical. Owing to its good delignification capability and relatively low price, in relation to its high specific oxidation potential, ozone is a costeffective complement to other chemicals in bleaching sequences, in which no chlorine chemicals are used. It is difficult by these sequences to achieve long range bleaching without serious carbohydrate degradation, which deteriorates the strength of the fiber material.

Ozone, on the whole, causes considerable degradation, which distributes itself between moderate direct carbohydrate degradation and alkali sensitivity, due to the introduction of carbonyl groups into the cellulosa, which causes rapid degradation in a subsequent alkaline step. Due to the alkali sensitivity, the value obtained at the viscosity analysis is lower than what corresponds to real polymerisation degree of the carbohydrate material. The higher real polymerisation degree is determined simply by a boron hydride reduction of the pulp before the viscosity analysis. The total degradation in the ozone step would be reduced substantially, if boronhydride steps are introduced into the bleaching sequence

after the ozone step. For several reasons, this is practically not possible. Until now no applicable solution has been proposed, by which this alkali instability could be avoided.

5 Alternatives to ozone are peracids, such as per-
formic acid, peracetic acid and persulphate (Caros acid),
which at suitable conditions yield low carbohydride de-
gradation. Bleaching with these can be carried out in
10 existing equipment found in traditional bleach plants,
contrary to ozone. A serious disadvantage, however, is
that they are considerably more expensive than ozone, in
relation to their oxidation capability.

At the present intention the costeffective de-
lignification of ozone has been combined with a treatment
15 with a small amount of peracid, which was found to sub-
stantially reduce the alkali instability caused by the
initial ozone treatment of the pulp. The intention builds
on the fact that the combination step can be adapted to
the apparatur solution, which was presented for HC ozone
20 steps, see USA 5 181 989. It was shown that the relati-
vely limited peracid treatment, which is a prerequisite
of the actual combination step, can be carried out in the
normal treatment volume for more diluted pulp, in order
to extract soluble lignin at slightly increased pH and,
25 respectively, to treat the pulp with chelating agent in,
order to remove disturbing transition metals after the
ozone reactor, see patent SE 501 836.

Such combination step involves the difficulty
that the ozone treatment must be carried out at low tem-
30 perature and low pH, preferably 2-3, in order to be se-
lective, while the peracid treatment requires a relati-
vely high temperature and a higher pH, preferably 4-6.
Owing to the fact that the combination step, which is
carried out in a HC ozone step with subsequent dilution
35 to a MC system, requires smaller amounts of peracid,
because the emphasis is put on the ozone, it has been
possible to adapt the conditions to existing HC ozone

step equipment.

Figure 1 describes the system for this combination step. The apparatus equipment is entirely identical with that of a simple HC ozone step, with the exception of the charging equipment for peracid. Figure 1 includes ozone equipment 2, peracid charging equipment 3, a first press 1 and a second press 4.

Figures 2 and 3 illustrate the liquid and temperature balance according to the conditions used according to the invention.

Figures 4 and 5 show the effect of the kappa numbers (which illustrate the lignin content in the pulp) and, respectively, the effect on the pulp viscosity, both directly on the pulp and after a boron hydride reduction of the pulp.

The ozone treatment takes place at a pulp concentration of $> 35\%$ and a temperature somewhere between 20 and 60°C . This is a compromise between selectivity requirements, which are furthered by a very low temperature, and to cool the hot white water, without seriously deteriorating the washing efficiency etc. The ozone reaction is extremely rapid and, therefore, the dwell time in the ozone reactor is only one or a few minutes. The pulp is diluted with hot water of a higher pH to a pulp concentration of about 12% , and peracid is added. After a dwell time in a vessel of between 10 and 30 minutes, the pulp is washed. Charged peracid is consumed at a pH between 4 and 6 and a temperature of $60-80^{\circ}\text{C}$. Figure 4 shows the effect on the kappa number as a function of the consumption of ozone and, respectively, peracetic acid, both expressed as OXE (1 OXE = the substance amount, which takes up one mole of electrons at the reduction of the substance, 1 kg peracetic acid = 26.3 OXE, 1 kg ozone = 125 OXE). The peracetic acid yields a smaller, but more selective delignification contribution and substantially decreased alkali sensitivity, which at normal viscosity analysis, see Figure 5, yields an increased pulp visco-

sity, especially when the pulp is not boron hydride reduced before the analysis.

CLAIMS

1. A method of bleaching pulp in a combination step with ozone and peracid or salts thereof, such as peracetic acid, characterized in that the pulp is ozone treated in a HC step, the pulp is diluted with water or white water, and peracid or salts thereof, such as peracetic acid, are added, whereafter the pulp is treated in a MC bleaching tower.
2. A method according to claim 1, characterized in that the pulp is a sulphate pulp with kappa number from 3 to 15, preferably from 5 to 10.
3. A method according to claim 1 or 2, characterized in that the amount of ozone added in the HC step is between 0.5 and 10 kg ptp, preferably between 1.5 and 5 kg ptp.
4. A method according to any of claims 1-3, characterized in that the amount of added peracetic acid is between 1 and 10 kg ptp, preferably between 2 and 6 kg ptp.
5. A method according to any of claims 1-4, characterized in that the pulp being treated has a kappa number in the range of 6.5-8, the ozone amount is in the range of 2-4 kg ptp, and the peracetic acid amount is in the range of 2.5-5 kg ptp.
6. A method according to any of claims 1-5, characterized in that the temperature in the ozone step is between 20 and 60°C, preferably between 40 and 50°C.
7. A method according to any of claims 1-6, characterized in that the temperature in the peracetic acid step is above or equal to 60°C, preferably 80°C.

6

8. A method according to any of claims 1-7, characterized in that the dwell time in the peracetic step is at least 10 minutes, 15-30 minutes.

5

AMENDED CLAIMS

[received by the International Bureau on 3 December 1996 (03.12.96);
original claims 1, 3 and 4 amended; remaining claims
unchanged (2 pages)]

1. A method of bleaching pulp in a combination step with ozone and peracid or salts thereof, such as peracetic acid, characterized in that the pulp is ozone treated in a High Consistency step, the pulp is diluted with water or white water, and peracid or salts thereof, such as peracetic acid, are added in an amount between 0.5 and 10 kg ptp, whereafter the pulp is treated in a Medium Consistency bleaching tower.
2. A method according to claim 1, characterized in that the pulp is a sulphate pulp with kappa number from 3 to 15, preferably from 5 to 10.
3. A method according to claim 1 or 2, characterized in that the amount of ozone added in the High Consistency step is between 0.5 and 10 kg ptp, preferably between 1.5 and 5 kg ptp.
4. A method according to any of claims 1-3, characterized in that the amount of added peracetic acid is between 2 and 6 kg ptp.
5. A method according to any of claims 1-4, characterized in that the pulp being treated has a kappa number in the range of 6.5-8, the ozone amount is in the range of 2-4 kg ptp, and the peracetic acid amount is in the range of 2.5-5 kg ptp.
6. A method according to any of claims 1-5, characterized in that the temperature in the ozone step is between 20 and 60°C, preferably between 40 and 50°C.
7. A method according to any of claims 1-6, characterized in that the temperature in the peracetic acid step is above or equal to 60°C, preferably 80°C.

8. A method according to any of claims 1-7, characterized in that the dwell time in the peracetic step is at least 10 minutes, 15-30 minutes.

5

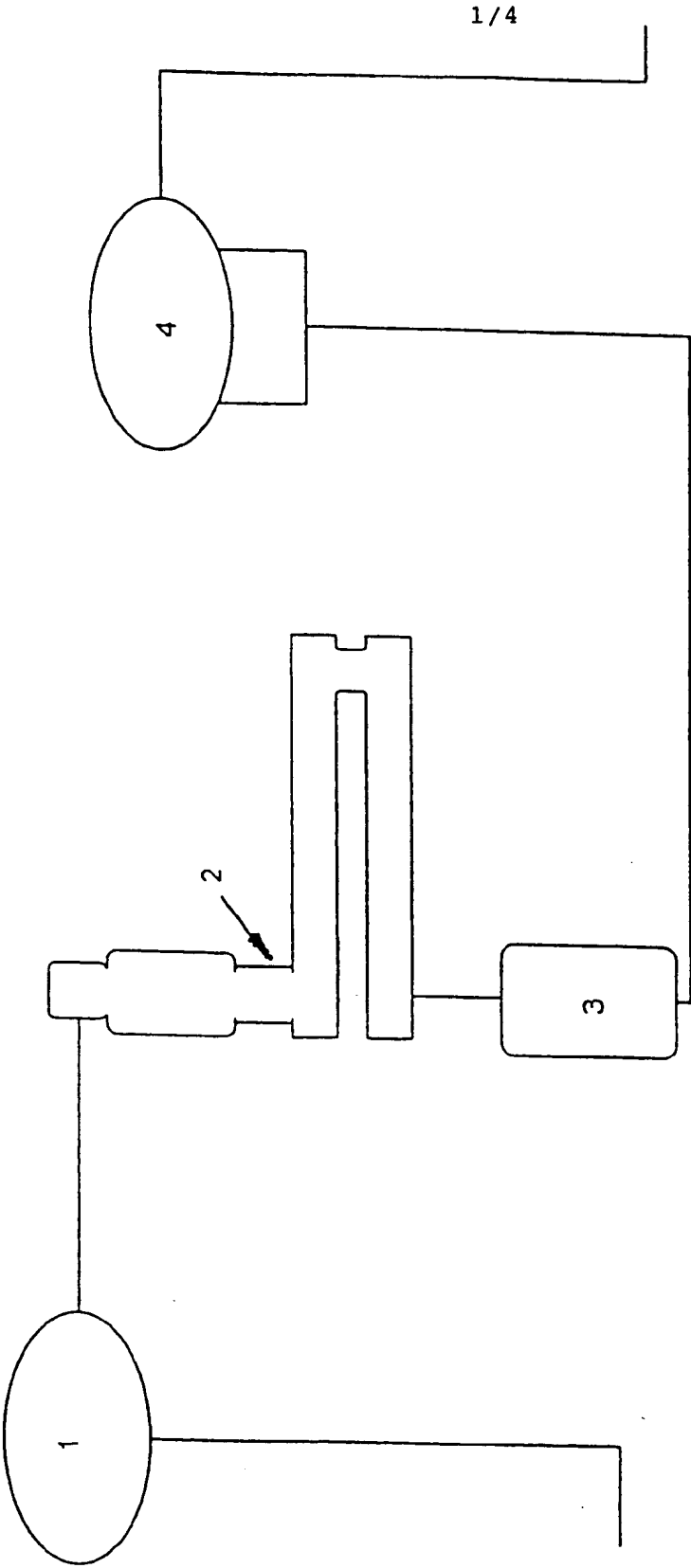


Fig 1

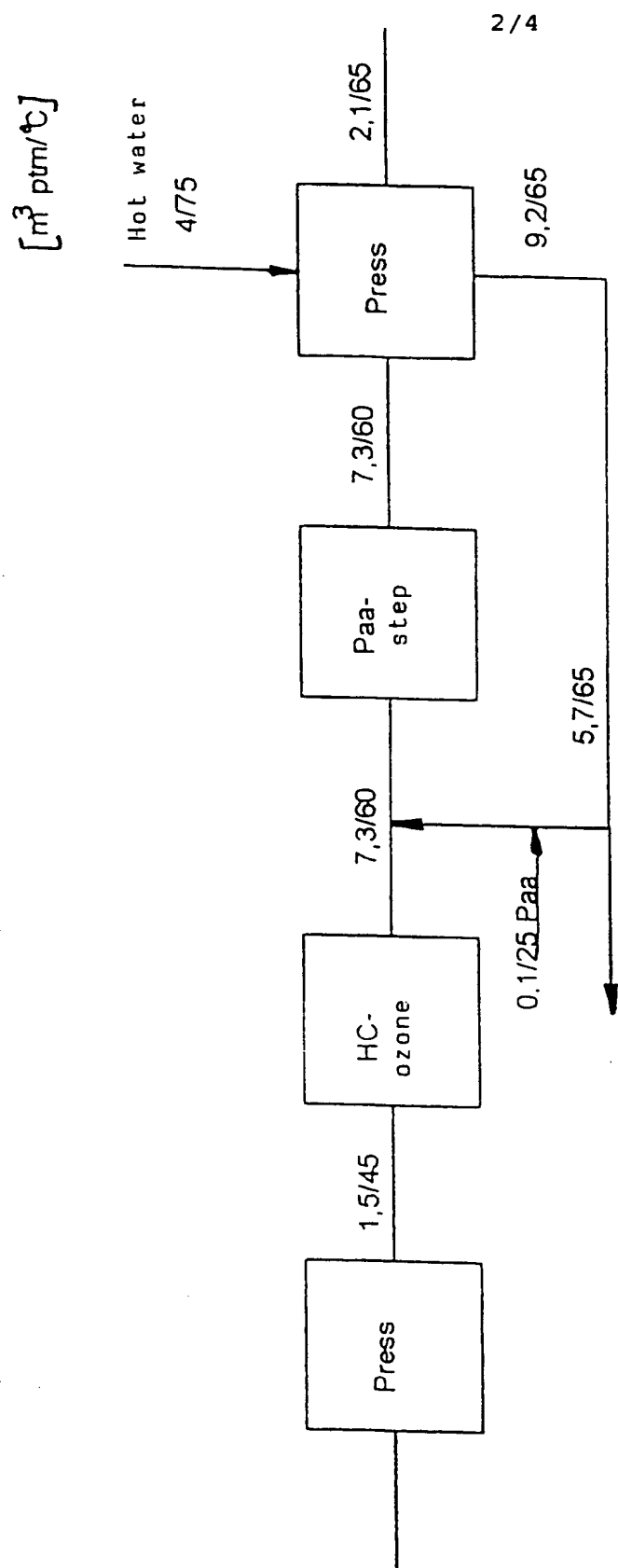


Fig 2

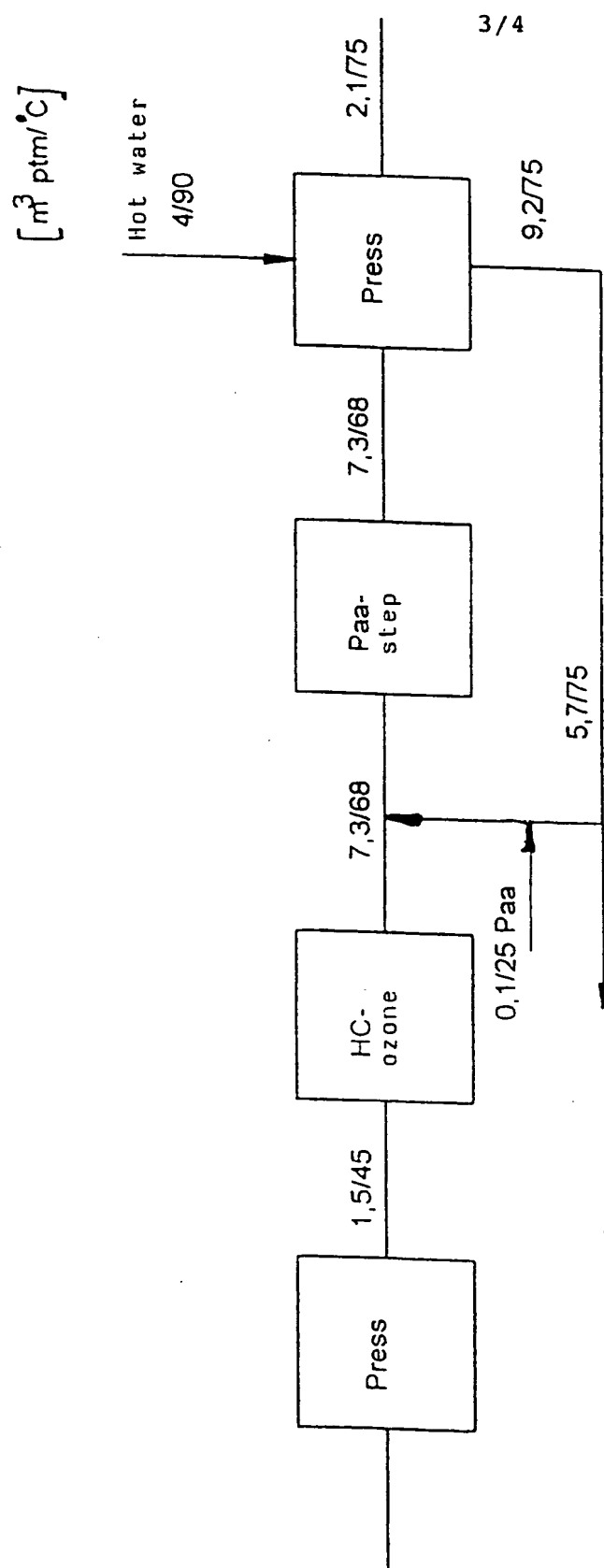


Fig 3

4/4

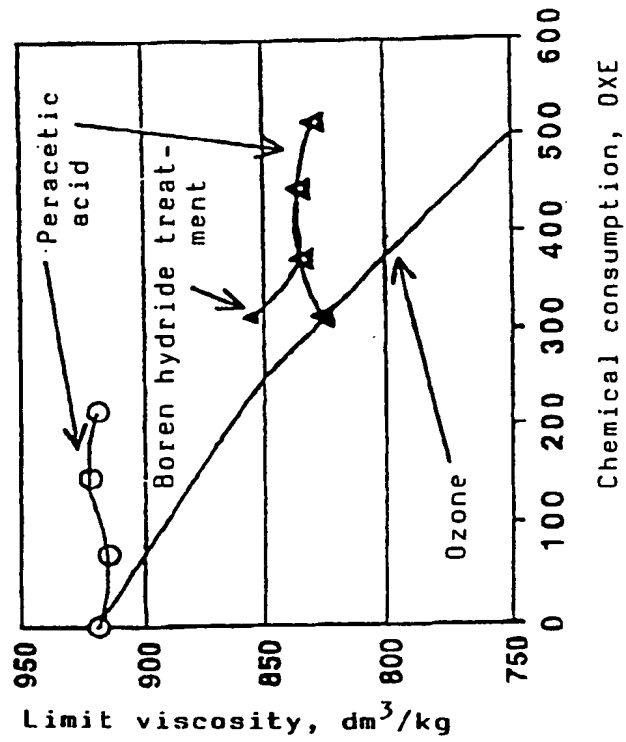


Fig 5

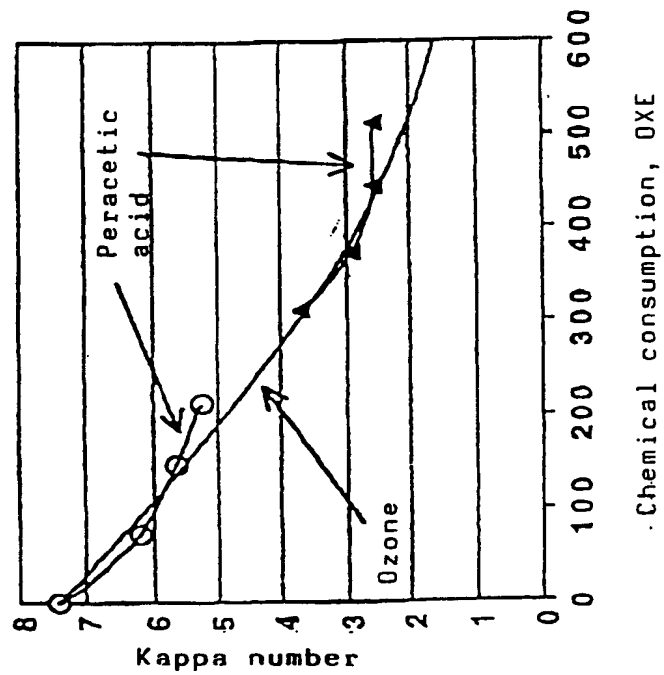


Fig 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 96/00882

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 9/153, D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9221814 A1 (INTEROX INTERNATIONAL), 10 December 1992 (10.12.92), page 10, line 12 - page 11, line 11 --	1-3, 6-8
A	FR 2692917 A1 (L'AIR LIQUIDE), 31 December 1993 (31.12.93) -- -----	1-8

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

1 October 1996

Date of mailing of the international search report

07-10-1996

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Marianne Bratsberg
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

05/09/96

International application No.

PCT/SE 96/00882

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9221814	10/12/92	AT-T- 127179	15/09/95
		AU-B- 651462	21/07/94
		AU-A- 1877592	08/01/93
		BE-A- 1004974	09/03/93
		BR-A- 9206112	10/10/95
		CA-A- 2110698	10/12/92
		DE-D,T- 69204457	18/04/96
		EP-A,B- 0587822	23/03/94
		SE-T3- 0587822	
		ES-T- 2079209	01/01/96
		FI-D- 935422	00/00/00
		JP-T- 6507683	01/09/94
		NO-A- 934406	26/01/94
		NZ-A- 242996	27/01/95
FR-A1- 2692917	31/12/93	NONE	